Effect of Pressure on the Band Structure of Zinc-Sulphide Using LUC-INDO Calculations

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Abstract

We study the electronic and structure properties of zinc-sulphide (ZnS) under high pressure, using large unit cell method. We employ intermediate neglect of differential overlap calculation, with appropriate corrections to the band gap and zero point energy to the cohesive energy. The results are in reasonable agreement with available experimental data. The effect of pressure on zinc-sulphide causes the following effect; an increase of band gap, valence bandwidth and the cohesive energy, and a decrease of the conduction bandwidth. This model is predicted a decrease of the electronic occupation probability for the s and p orbital of sulfur with an increase of this probability for the s-orbital of zinc with increase of pressure.

Keywords : ZnS, high pressure, band structure, semiempirical methods, LUC-INDO.

تأثير الضغط على التركيب ألحزمي لكبريتيد الخارصين باستعمال حسابات الإهمال المتوسط للتداخل التفاضلي لخلية الوحدة الكبيرة

الخلاصة

تم في هذا البحث دراسة الخواص الالكترونية والتركيبية لكبريتيد الخارصين (ZnS) تحت تأثير الضغوط العالية باستعمال طريقة خلية الوحدة الكبيرة. حيث تم استخدام حسابات الإهمال المتوسط للتداخل التفاضلي مع إجراء تصحيحات مناسبة لفجوة الطاقة، وطاقة نقطة الصفر إلى طاقة الترابط. النتائج التي تم الحصول عليها كانت متطابقة إلى حد مقبول مع النتائج العملية المتوفرة . تأثير الضغط على البلورة قيد الدراسة أدى إلى التأثيرات التالية: زيادة كل من فجوه الطاقة وعرض حزمة التكافؤ وطاقة الترابط، ونقصان عرض حزمة التوصيل. إن هذا النموذج يتوقع نقصان احتمالية وجود الالكترونات في المدارين s و p للكبريت مع زيادة هذه الاحتمالية للمدار s في الخارصين بزيادة الضغط المسلط.

1 Introduction

Calculation of the bulk ground state properties, such as lattice constants, bond lengths, bulk modulus, cohesive energy, and atomic position, play an important role in the physics of condensed matter [1-3]. Bulk calculations help us to understand, characterize, and predict mechanical properties of materials in surroundings, under extreme conditions, as in geological formations and settings, and for industrial applications. Crystalline materials come in many different structure and in contrast to isotropic materials, the description of the ground state of crystalline may in general need multiple lattice parameters and an atomic basis.

In recent years, several theoretical and experimental studies have focused on the electronic properties of ZnS semiconductor largely motivated by the potential applications of these materials in opto-electronic devices, particularly blue-green lasers [4], and in technological applications mainly in the field of optical devices.

In this work we have studied the effect of pressure on the some properties of zinc - sulphide (ZnS) in the zinc-blende phase using the self-consistent LUC-INDO method in the linear combination of atomic orbitals approximation [5,6]. This method, which had been already successfully employed for a long time in molecular theory has gained wide acceptance in calculations of the electronic structures of crystals.

2 Structural Properties and Phase Transition of ZnS

Zinc sulphide crystallizes under normal transition with the zinc-blende (ZB) structure [7,8], in the fourfold-coordinated which corresponds to the space group ($\Gamma\bar{A}3m$). As the pressure is applied to ZnS it transforms into rock-salt phase (NaCl) with six-fold coordinated Smith and Martin [9] reported a transition pressure of 11.7 GPa, although later studies have placed it at a somewhat higher pressure 14.5 GPa according to Nelmes and McMahon [10] and 15.5 GPa according to Uchino et al [11]. In contrast to zinc-blende structure, the NaCl phase is found to an indirect-gap semiconductor [12.13], which has been confirmed by a first - principles calculations [14]. At pressure about 65 GPa the NaCl phase has been reported to undergo a Cmcm–like distortion with no significant change in volume [10,15]. The high pressure behavior of ZnS has been the subject of several recent theoretical [8, 16] and experimental [15].

3 Computational Details

The basic idea of the large unit cell is in computing the electronic structure of the unit cell extended in a special manner at k=0 in the reduced Brillouin zone. This equivalent to a band structure calculation at those k-point; which transform to Brillouin zone center on extending the unit cell [17]. Using the LCAO, the crystal wavefunction in the LUC-INDO formalism is written in the following form:

$$\psi_a(k,r) = \sum_u^{cells} \sum_p^{basis} \exp(ikR_u) C_{pa}(k) \phi_p(r - R_u) \qquad (1)$$

Where C_{pa} are the orbital expansion coefficients and the R_u is the lattice translation vector. The atomic orbital used for the LCAO procedure form the basis set of the calculation. We expand the wavefunction in a set of Slater-type orbitals (STO) [18]. This is very efficient basis set, these orbitals have the radial form:

$$R_{nl}(r) = \frac{(2\zeta)^{n+1/2}}{(2n!)^{1/2}} r^{n-1} \exp(-\zeta r) \qquad (2)$$

Where ζ the orbital exponent. The expectation value of the electronic energy is:

$$\varepsilon = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \qquad (3)$$

The Hamiltonian for a microcrystal consisting of N electrons may be written as

$$H = \sum_a^N \left(-\frac{1}{2} \nabla_a^2 - \sum_A^{n_A} Z_A r_{AA}^{-1} \right) - \frac{1}{2} \sum_a^N \sum_p^N r_{ap}^{-1} + \sum_A^{n_A} \sum_B^{n_B} Z_A Z_B R_{AB}^{-1} \qquad (4)$$

Where Z_A is the core charge, R_{AB} is the distance between the atoms A and B, and the summation is over all nuclei. But the Roothaan-Hall equations can be obtained [19]:

$$\sum_p (F_{pqk} - \varepsilon_a S_{pqk}) C_{pqk} = 0 \qquad (5)$$

F_{pqk} represents the Fock matrix elements and S_{pq} is the overlap integral for atomic function ϕ_q and ϕ_P, and written as :

$$S_{pqk} = \sum_{u} \left\langle \phi_p\left(r - R_0\right) \middle| \phi_q\left(r - R_u\right)\right\rangle \exp\left(ikR_u\right) \tag{6}$$

The Fock matrix elements may be represent as the sum of the one- and two- electron components:

$$F_{op,uq} = \left\langle \phi_p^1(1) \left| -\frac{1}{2}\nabla_1^2 - \sum_a Z_a r_{1a}^{-1} \right| \phi_q^u(1) \right\rangle + \sum_{v,\lambda}^{cell} \sum_{rs}^{basis} P_{rs}^{v\lambda}\left((\phi_p^o \phi_q^u | \phi_r^v \phi_s^\lambda) - \frac{1}{2}(\phi_p^o \phi_r^v | \phi_s^\lambda \phi_q^u)\right) \tag{7}$$

$P_{rs}^{v\lambda}$ is the density element with the form:

$$P_{rs}^{v\lambda} = 2\sum_{k'} \sum_{a}^{occ} C_{rak'}^{*} C_{sak'} \exp\ ik'.(R_\lambda - R_v) \tag{8}$$

In the equation (5) if k=0 then

$$\sum_{p} (F_{pq0} - \varepsilon_a S_{pq0}) C_{pq0} = 0 \tag{9}$$

In the INDO approximation one can utilize that many of the integrals are very small or zero and begin to neglect systematically some of the matrix elements and many approximations can be made. The Fock matrix elements in their final forms in the LUC-INDO formalism are used in this work [5]:

$$\begin{aligned} F_{pp(0)} = U_{op,op} - \sum_{A\neq B}\sum_{v} Z_B \gamma_{AB}^{ov} + \sum_{v} \beta_A^0 (S_{op,vp} - \delta_{ov}) + \sum_{r}\sum_{v} P_{rr}(0)\gamma_{AB}^{ov} - \\ \frac{1}{2}\sum_{v\neq 0} P_{pp}(0) f(x) \gamma_{AA}^{ov} - \frac{1}{2}\sum_{r} P_{rr}(0)(\phi_p^r \phi_r^o | \phi_p^o \phi_r^o) \end{aligned} \tag{10}$$

$$F_{pq(0)} = \sum_{v} \beta_{AB}^0 S_{op,vp} - \frac{1}{2}\sum_{v} P_{pq}(0) f(x) \gamma_{AB}^{ov} \tag{11}$$

For p and q on different atomic centers, and

$$F_{pq(0)} = \sum_{v} \beta_A^0 S_{op,vp} - \frac{1}{2}\sum_{v\neq 0} P_{pq}(0) f(x)\gamma_{AA}^{ov} + \frac{1}{2}P_{pq}(0)[(\phi_p^o\phi_q^o|\phi_r^o\phi_s^o) - (\phi_p^o\phi_r^o|\phi_s^o\phi_q^o)] \tag{12}$$

For p and q on the same atomic center, □□□ is the bonding parameter and □$_{AB}$ is the average electrostatic repulsion between any electron on atom A and any electron on atom B, and U_{pp} is the local core matrix element and can be written as:

$$U_{pp} = -\frac{1}{2}(I_p + A_p) + (Z_A - \frac{1}{2})\gamma_{AA} \tag{13}$$

Where I_p and A_P are the ionization potential and electron affinity, respectively, *f(x) is* the modulating function and is given by [20]

$$f(x) = (\frac{\sin x}{x})^2 \quad (14)$$

For the 8 atom LUC x is given by

$$x = \frac{\pi R_{AB}}{a} \quad (15)$$

R_{AB} is the distance between the atom A at the central lattice o and the atom B at the v lattice.

4 The Results and Discussion

4.1 Choice of Parameters

The empirical parameters in the LUC–INDO method are the orbital exponent ζ, the bonding parameter β, the electronegativity of s-orbital (E_s), and the electronegativity of p-orbital (E_p). The value of the orbital exponent determines the charge distribution of electrons around the nucleus or in the solid. These parameters are varied firstly to give nearly the exact value of the equilibrium lattice constant, cohesive energy, indirect band gap and valence band widths. The optimum values of these parameters used for ZnS in the present work are listed in Table 1.

Table 1. Parameters sets of ZnS used in this work.

Parameter	Zn	S
ζ (a.u)$^{-1}$	2.0038	2.112
β_{AB} (eV)	-17.17	-20.23
E_s (eV)	15.57	19.43
E_p (eV)	6.97	8.26

The results of cohesive energies as a function of lattice constant are obtained by the above method at 0 k and zero pressure. The equilibrium lattice constant obtained from LUC-INDO calculation for ZnS is listed in Table 2 in comparison with experimental and other results. The lattice constant for ZnS presented here is slightly smaller than experimental calculations, the difference

between the experimental data and our results are very small, i.e., only 0.03 Å. Figure 1 is fitted to the Murnaghan's equation of state [21], from which we obtain the equilibrium lattice parameter a_0, the bulk modulus B, and its derivative B'_0.

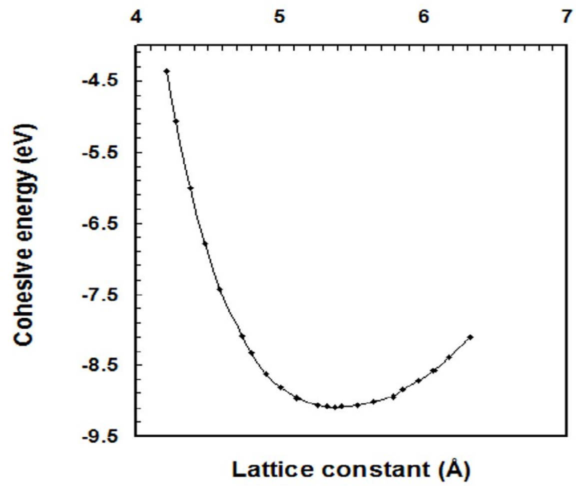


Figure 1. Cohesive energy as a function of lattice constant for ZnS.

Based on the calculations, we obtained the cohesive energy value of the present work is in good agreement with experimental results (as shown in Table 2). We added the free atom sp shell energy (E_{free}), for the cohesive energy to correct its value. In this work E_{free} =151.86 eV, and this value is taken from ionization potential of ZnS, On the other hand, the zero-point vibration energy (E_0) is neglected because its very small = 0.085 eV. The calculated direct bandgap is listed in Table 2 and the differences between LUC-INDO and experimental result of direct bandgap is relatively small, where the bandgap values is higher than experimental values this is, mainly, a consequence of two approximations made in this calculation. First, the core structure was ignored, through some compensation results from using semiempirical parameters . Second, using minimal basis set atomic orbitals (without considering any excited levels). The calculated bulk modulus of ZnS is 74 GPa, which is in good agreement with experimental value of 76.9 GPa [22], and 79.5 GPa [23]. Hybridization state show an increasing s-state occupation with the decreasing atomic number of the compound where the occupation of s of sulfur is larger than of that for zinc.

The eigenvalues of the high symmetry point are shown in Table 3.

Table 2. Electronic and structural properties calculated within the large unit cell at ground state (zero pressure and 0 temperature).

Property	Present work	Experimental	Others
Lattice constant (Å)	5.381	5.411 [24]	5.30 [25], 5.35 [26]
Cohesive energy (eV)	9.08	8.97 [27]	7.4 [28], 8.33 [29]
Conduction bandwidth (eV)	1.89	.....	.....
Valence bandwidth (eV)	12.45	.....	.....
Band gap (eV)	4.242	3.82 [30]	3.24 [31], 3.98 [32]
Hybridization state of S	$s^{1.86}p^{4.53}$	s^2p^4	.....
Hybridization state of Zn	$s^{1.65}$	s^2	.....

Table 3. Eigenvalue of ZnS at high symmetry point, compared with other result.

Symmetry point	**Eigenvalue (eV)**	
	Present	**Reference (25)**
Γ_{1v}	-12.45	-13.51
Γ_{15v}	0	0
Γ_{1c}	4.242	2.15
Γ_{15c}	7.32	6.49
X_{1v}	- 11.12	- 12.05
X_{5v}	- 4.51	- 4.87
X_{1c}	4.34	3.18
X_{4c}	6.23	4.02

4.2 The Effect of Pressure on the Properties

The effect of pressure on the electronic structure and other properties can be calculated from the present theory and computational procedure**.** By the use of our calculated values of the bulk modulus B, and its derivative volume change (V) with applied pressure was calculated using the following equation [33,34]:

$$P = \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right] \qquad (16)$$

Where P is pressure, and V_0 is the equilibrium volume at zero pressure. We applied a pressure up to 14 GPa, because this structure transforms to another phase, rock salt (NaCl), when pressure exceeds nearly 14 GPa [10]. The calculated lattice constant as a function of pressure is shown in Fig.2.

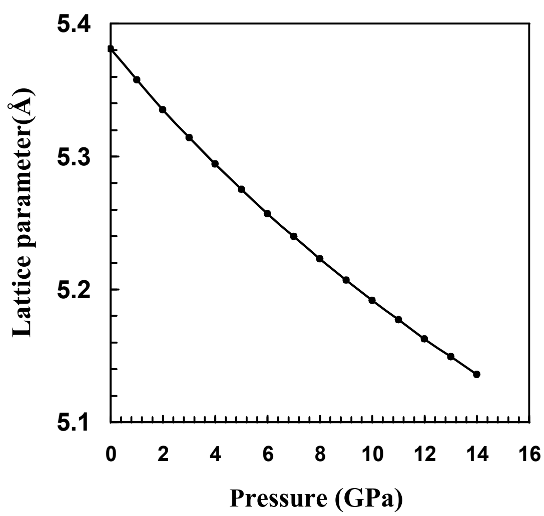


Figure 2. Lattice constant as a function of pressure using LUC – INDO model.

The pressure dependence of the cohesive energy is illustrated in Fig. 3. It is shown that the absolute value of the cohesive energy decreases as the pressure increases.

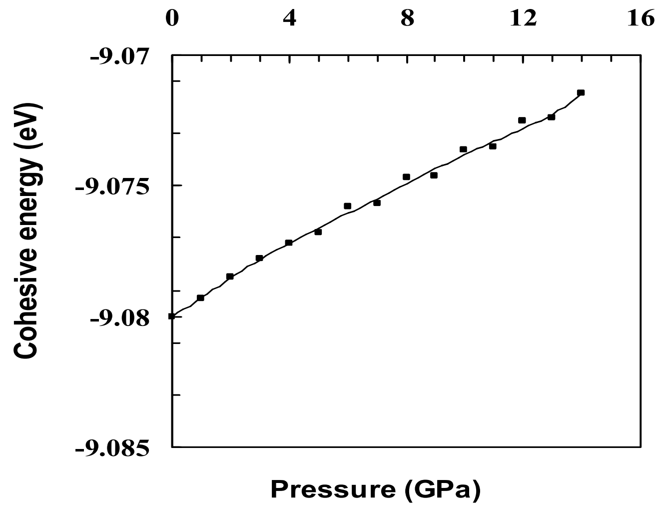


Figure 3. Cohesive energy versus pressure for ZnS.

The pressure derivative of the high symmetry points (Γ_{1v} , Γ_{15v} , X_{1v} , X_{5v} , X_{1c}, X_{5c} , Γ_{15c} , and Γ_{1c}) is shown in table 4. From this table one can see that the eigenvalues at conduction band (X_{5c}, Γ_{15c} , Γ_{1c}, X_{1c}) are increase with pressure, whereas eigenvalues at valence band (X_{5v} , X_{1v} , Γ_{1v}) decrease with pressure, However, the decrease of X_{5v} , X_{1v} , and Γ_{1v} with pressure is small.

Table 4 . The pressure derivative of the high symmetry points**,** where the minus sign mean that the high symmetry point decrease with pressure effect.

Symmetry point	The pressure derivative (meV/GPa)
Γ_{1v}	-18.6
Γ_{1c}	51.22
Γ_{15c}	27.7
X_{1v}	-21.3
X_{5v}	-15.2
X_{1c}	43.04
X_{4c}	31.2

The pressure derivative of the direct bandgap is shown in figure 4, from this figure we can see that the direct band increase with the increase of pressure. The predicted effect of pressure on the valence bandwidth, and conduction bandwidth is illustrated in Figures 5 and 6, respectively. The valence bandwidth increase with the increase of pressure, while the conduction bandwidth decreases with the increase of pressure.

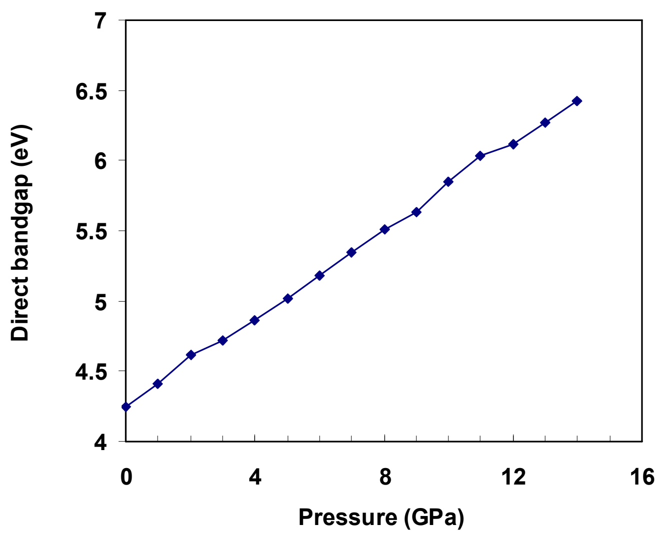


Figure 4 . The effect of pressure on the bandgap.

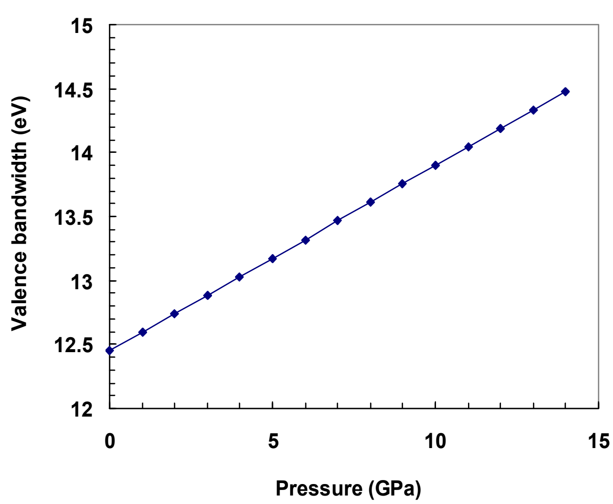


Figure 5. Pressure dependence of the valence bandwidth of ZnS.

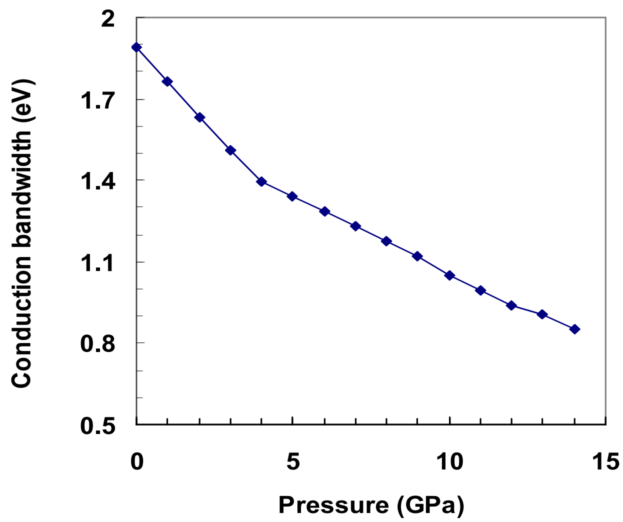


Figure 6. Predicted effect of pressure on the conduction bandwidth.

We found that the s and p state occupation for S decreases with the increase of pressure, whereas the s states occupation for Zn increases in this case. The occupation of s and p states for S and Zn with pressure is shown in Fig.7. The increase of pressure causes an increase of the probability of electron transition from sulfur to zinc. This is known and leads to a phase transition due to the change of electronic distribution such as the s-d transition in alkali metals [35].

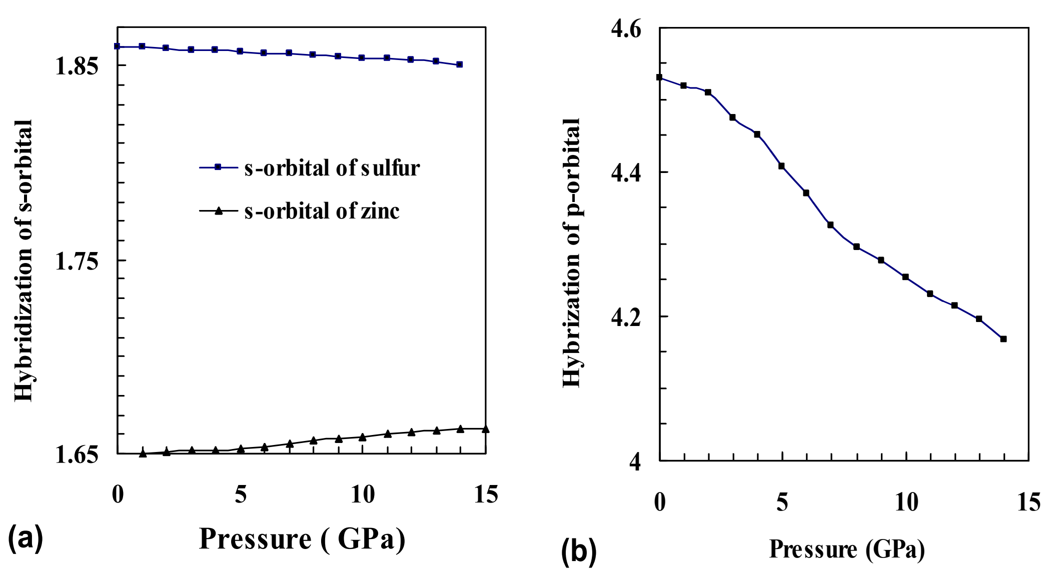


Figure 7. The effect of pressure on the hybridization of (a) s- state and (b) p- state.

Conclusions

In conclusion, we applied large unit cell within the intermediate neglect of differential overlap method to studies the structure and electronic properties of ZnS semiconductor under the effect of pressure. The properties obtained are in very good agreement with the existing experimental data and with GDSP/DFT except the direct bandgap which is greater than the experimental data, this difference is due to the neglect to the core states and to the approximations incorporated with the computational formalism.

References

[1] E, Schröder, Phys. Rev. E 62, 8830 (2000).

[2] C. Person and E. Jenzen, J. Phys. Condens. Matter 10, 10549 (1998).

[3] E. Wachowicz and A. Kiejna, J. Phys.:Condens. Matter 13, 10767 (2001)

[4] B. S. Wherrett, J. Cryst. Growth 159, 766 (1996).

[5] A. H. Harker and F. P. Larkins, J. Phy. C : Solid State Phys. **12**, 2487, (1979).

[6] I. O. Radi ,M. A. Abdulsattar, and A. M. Abdul-Lettif, phys. stat. sol. (**b**) **244**, 1304 (2007).

[7] J. López-Solano, A. Mujica, P. Rodríguez-Hernández, and A.Muńoz, Phys. Status Solidi B **235**, 452 (2003).

[8] A. Mujica, A. Rubio, A. Muńoz,, and R. J. Needs, Rev. Mod. Phys. 75, 863 (2003).

[9] P. L. Smith, and J. E. Martin, Phys. Lett. **19**, 541 (1965).

[10]R.J. Nelmes, andM. I. McMahon, 1998, Semicond. Semimetals **54**, 145 (1998).

[11] M. Uchino, T. Mashimo, M. Kodama, T. Kobayashi, E. Takasawa, T. Sekine, Y. Noguchi, H. Hikosaka, K. Fukuoka, Y. Syono, T. Kondo, and T. Yagi, J. Phys. Chem. Solids **60**, 827 (1999).

[12] S. Ves, U. Schwarz, N. E. Christensen, K. Syassen, and M. Cardona, Phys. Rev. B **42**, 9113 (1990).

[13] Y. H. Zhou, A. J. Campbell, and D. L. Heinz, J. Phys. Chem. Solids **52**, 821 (1991).

[14] J. E. Jaffe, R. Pandey, and M. J. Seel, Phys. Rev. B **47**, 6299 (1993).
[15] S. Desgreniers, L. Beaulieu, and I. Lepage, Phys. Rev. B **61**, 8726 (2000).
[16] A. Qteish, and A. Muńoz, phys. stat. sol. (b) **223**, 417 (2001).
[17] B. J. Craig and P. V. Smith , phys. stat. sol. (b) **140**, 491, (1987) .
[18] J. Slater , "Quantum Theory of Atomic Structure" , McGraw – Hill , (1974).
[19] R. Evarestov and V. Lovchikov, phys. stat. sol. (b) ,**79**, 743, (1977) .
[20] J. E. Szymanski , "Semiempirical Methods of Total Energy Calculations", Ph. D. , University of York , (1984).
[21] F. D. Murnaghan, Proc. Natl, Acad. Sci, USA **50**, 697(1944).
[22] Semiconductor, Physics of II-IV and I-VII Compounds, Semimagnetic Semiconductors, edited by O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 17, (Springer- Verlag, Berlin, 1982).
[23] S. Desgreniers, L. Beaulicu, and I. Lepage, Phys. Rev. B 61, 8726 (2000).
[24] N. Kh. Abrikosov, V. B. Bankina, L. V. Poretskaya, L. E. Shelimova, and E. V. Skudnova, *Semiconducting II-VI, IV-VI, and V-VI Compounds* (Plenum, New York 1969), p. 2.
[25] X. Chen, X. Hua, J. Hu, J. Langlois, and W. A. Goddard III, Phys. Rev. B 53, 1377 (1996).
[26] C.-Y. Yeh, W. Lu, S. Froyen, and A. Zunger, Phys. Rev. **B** **46**,10 086 (1992).
[27] R.Weidemann, H. Gumlich, M. Kupsch,H-U Middelmann, and U Becker, Phys. Rev. B 45, 1172 (1992).
[28] W. Louie, S. Ismail-Beigi, M. L. Cohen, and S. G. Louie, Phys. Rev. **B** 66, 195215 (2002).
[29] M. Oshikiri, and F. Aryasetiawan, Phys. Rev. B 60, 10754 (1999).
[30] W. H. Strehlow and E. L. Cook, J. Phys. Chem. Ref. Data **2**, 163 (1973).
[31] T. Kotani, and M. van Shilfgaarde, Solid State Commun. 121, 461 (2002).

[32] O. Zakharov, A. Rubio, X. Blase, M. L. Cohen, and S. G. Louie, Phys. Rev. **B** 50, 10780 (1994).
[33] S. Q. Wang and H. Q. Ye, J. Phys. : Condens. Matter , 17, 4475, (2005) .
[34] S. Q. Wang , H. Q. Ye and S. Yip , J. Phys. : Condens. Matter , 18, 395, (2006) .
[35] K. Takemura, and k. Syassen, Phys. Rev. B **28** , 1193 (1983).